

# Sol-Gel Processing of Functional and Structural Ceramic Oxide Fibers

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**Abstract.** Structural ceramic oxide fibers like  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub> (spinel), Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YAG) and eutectic Al<sub>2</sub>O<sub>3</sub>-Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> as well as the functional Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub> (PZT) fibers were successfully prepared by sol-gel processing. All precursors are based on metal oxohydroxopropionates. A comparative study of sol-gel routes leading to spinnable sols demonstrates the key role of propionic acid as an excellent agent for controlling hydrolysis and condensation reactions.

**Keywords:** ceramic fibers, spinnability, sol-gel

## 1. Introduction

Distinct preparation routes have been developed to achieve spinnable precursors of both structural [1–8] and functional ceramic fibers [9–14] using aqueous oxide sols and filament forming polymers as well as metals, metal salts, metal alkyls, alkoxides or carboxylates. In this study the preparation of similar spinnable precursors of both structural ceramic systems like  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub> (spinel), creep resistant Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YAG) and eutectic Al<sub>2</sub>O<sub>3</sub>-Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> as well as the functional piezoceramic Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub> (PZT) is presented and compared. All precursors are based on metal oxohydroxopropionates. Structural ceramic fibers offer distinct applications as reinforcing components. Piezoelectric fibers have potential applications in multifunctional composites as sensor and actuator materials.

## 2. Experimental

The preparation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> fibers can be started according to a sol-gel process as already described [7]. The reactions were carried out at room temperature. First aluminum sec-butoxide was reacted with different 2-alkoxyethanols such as methoxy- or isopropoxyethanol in an alcoholysis step. Then the modified aluminum sec-butoxide was reacted with propionic acid and finally water was added. This step was accompanied by a sharp increase of the sol viscosity

leading to a spinnable solution even without removing volatile components in a final concentration step. In order to investigate the alcoholysis step, the released sec-butanol was quantified by gas chromatography after distillation.

The processing of spinnable alumina sols was modified to obtain precursors of the stoichiometry of both Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (YAG) and eutectic Al<sub>2</sub>O<sub>3</sub>-Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>. Aluminum sec-butoxide was reacted during the alcoholysis step with methoxyethanol, which contained yttrium methoxyethoxide. In the case of MgAl<sub>2</sub>O<sub>4</sub> (spinel) instead of pure propionic acid a solution of magnesium carboxylate prepared from MgO was added to the aluminum compound in the second step of the process. After hydrolysis and a partial removal of volatile components, spinnable sols are obtained.

A spinnable Pb(Zr<sub>0.53</sub>Ti<sub>0.47</sub>)O<sub>3</sub> (PZT) precursor was prepared as already described [14] by adding excess propionic acid to a mixture of zirconium *n*-propylate and titanium ethylate. After addition of PbO dissolved in propionic acid or lead acetate trihydrate the clear solution was concentrated by evaporation of the volatile components leading to a solid, which melts by heating to 150°C.

## 3. Results and Discussion

### 3.1. Preparation of Non-Gelling Metal Carboxylates

In order to get highly viscous, spinnable sols the metal alkoxides used must be hydrolyzed without the

formation of gels. Therefore, the metal alkoxides need to be stabilized against gelation during hydrolysis. Suitable complexing agents are  $\beta$ -diketones, ketoesters or carboxylic acids. The latter are preferred due to the formation of strong intermolecular hydrogen bonding after hydrolysis, supposed to be decisive for drawing fibers from sols. The reaction of aluminum alkoxides with short chained carboxylic acids, however, yield hardly soluble and infusible compounds, which are unusable in sol-gel processes. This problem was avoided by the alcoholysis of aluminum sec-butoxide using 2-alkoxyethanols as modifiers [7].  $^{13}\text{C}$  NMR resonances of  $\text{CH-O}$  and  $\text{CH}_2\text{-O}$  after alcoholysis and the evolution of the  $\text{Al}^{\text{VI}} : \text{Al}^{\text{IV}}$  ratio measured by  $^{27}\text{Al}$  NMR as a function of the ratio of isopropoxyethanol to aluminium sec-butoxide revealed the isopropoxyethanolate groups bonded to Al as monodentate ligands. The weakly nucleophilic ether oxygen has obviously been kept from interfering with the Al coordination sphere in presence of the released sec-butanol. The alcoholysis reaction of aluminum sec-butoxide with 2-alkoxyethanols leads to  $\text{Al}(\text{OCH}_2\text{CH}_2\text{OR})_x(\text{OBu}^s)_{3-x}$  with  $1.5 \leq x \leq 3$  which was established by gas chromatography measurements of the volatiles. Alcoholysis converts the starting material into a compound, which results in a homogeneous solution after addition of an excess of short chained carboxylic acid like acetic or propionic acid. Thus, aluminum carboxylates were prepared, which are highly soluble in polar media. The modified aluminum sec-butoxide may be combined with heteromolecules forming homogeneous solutions.  $\text{Y}(\text{OCH}_2\text{CH}_2\text{OMe})_3$  dissolved in methoxyethanol may be added to  $\text{Al}(\text{OCH}_2\text{CH}_2\text{OR})_x(\text{OBu}^s)_{3-x}$  as purchased or  $\text{Mg}(\text{OOCeT})_2$  dissolved in propionic acid. The latter was prepared from  $\text{MgO}$  and propionic acid. The water released during this reaction may be used for hydrolysis of the carboxylated  $\text{Al}(\text{OCH}_2\text{CH}_2\text{OR})_x(\text{OBu}^s)_{3-x}$ .

In contrast to the behavior of aluminum sec-butoxide, the direct carboxylation of zirconium and titanium alkoxides leads to the well studied soluble zirconium and titanium alkoxycarboxylates [15–18]. The gelation time of these modified alkoxides has been increased considerably. The addition of excess propionic acid to a mixture of 0.53 mol  $\text{Zr}(\text{OPr}^i)_4$  and 0.47 mol  $\text{Ti}(\text{OEt})_4$  and subsequently water resulted in a loss of all alkoxy groups, while 1.6 mol propionic acid and 1.8 mol water were consumed according to IR investigations, analysis of volatiles by gas chromatography and Karl-Fischer titrations. The chemical

analysis of the solid residue suggests a compound consisting of  $\text{Zr}_{0.53}\text{Ti}_{0.47}\text{O}_{0.6}(\text{OH})_{1.2}(\text{OOCeT})_{1.6}$ . The solid is highly soluble in ethanol, in a mixture of propionic acid and  $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$  and fairly soluble in fused  $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$  (m.p.  $75^\circ\text{C}$ ). During heating,  $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$  converts to lead subacetate  $1/3\text{Pb}(\text{OAc})_2 \cdot 2/3\text{PbO}$ . The resulting PZT precursor consists of  $\text{Zr}_{0.53}\text{Ti}_{0.47}\text{O}_{0.6}(\text{OH})_{1.2}(\text{OOCeT})_{1.6}$  particles which are dispersed in a solution of fused lead subacetate at temperatures between  $100^\circ\text{C}$  and  $150^\circ\text{C}$ . So there is every reason to describe it as a sol. At room temperature the PZT precursor is a solid: a frozen sol.

Using these pathways just described sols after hydrolysis were obtained in all cases. Thus, an essential condition for the preparation of spinnable sols could be met.

### 3.2. Influence of Carboxylates on Spinnability

With regard to spinnability acetates and propionates differ considerably. In none of the systems listed in the experimental part the propionates could be completely replaced by acetates without losing spinnability by gelation. Merely in the case of PZT precursor a partial replacement was successful. Instead of lead propionate, prepared from  $\text{PbO}$  and propionic acid,  $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$  dissolved in propionic acid was effectively employed to prepare a melt-spinnable PZT precursor. By use of propionic acid all systems could be achieved as spinnable precursors. This emphasizes the significance of the alkyl chain which is only prolonged by one methylene group compared with acetate. This resulting ethyl chain serves as a spacer group sufficient to keep the molecular clusters apart from each other.

Decisive for the creation of spinnable precursors, however, is not only the use of propionic acid as carboxylation agent, but also the appropriate excess of propionic acid. Figure 1 (left) shows the IR spectra of the respective precursors and the corresponding bands in the carbonyl region. All systems may be spun if the concentration of propionic acid is adjusted properly. This concentration differs remarkably for the four systems. To obtain spinnability in the  $\text{Al}_2\text{O}_3$  system 3 mol equiv propionic acid are required. In the line YAG-spinel-PZT this amount decreases, being very small for PZT. This fact elucidates that propionic acid not only acts as a complexing agent, but also plays an important role as a solvent. The resulting metal oxohydroxocarboxylates are also solvated by propionic acid. This is

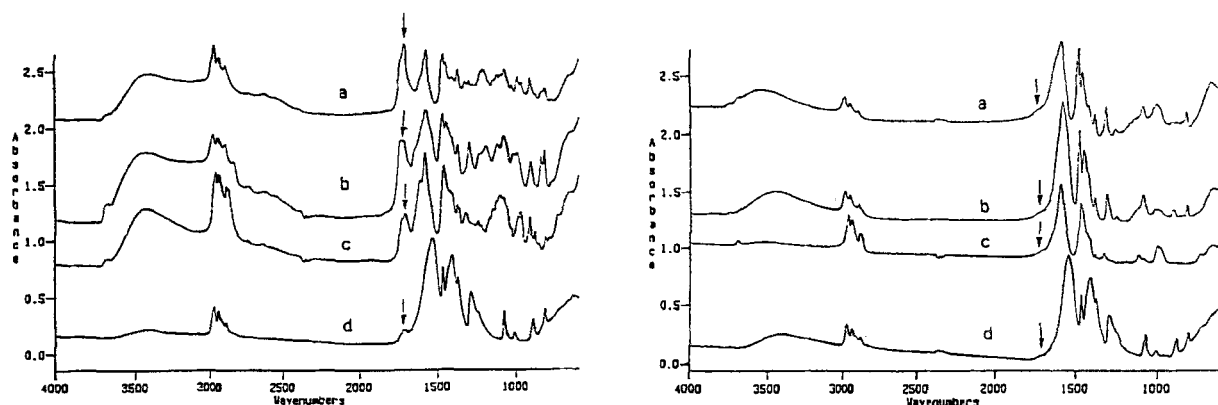


Figure 1. IR spectra of spinnable solutions (left) in the systems of  $\text{Al}_2\text{O}_3$  (a),  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (b),  $\text{MgAl}_2\text{O}_4$  (c),  $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$  (d) and IR spectra (right) of the gel fibers, respectively. Arrows indicate the region of carbonyl vibrations.

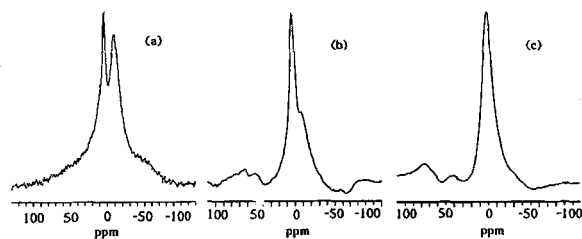


Figure 2.  $^{27}\text{Al}$  MAS-NMR measurements of a spinnable sol of the  $\text{Al}_2\text{O}_3$  system (a), gel fibers dried at  $80^\circ\text{C}$  (b) and gel fibers heated at  $200^\circ\text{C}$  (c).

evident in the  $\text{Al}_2\text{O}_3$  system. Figure 2(a) shows a  $^{27}\text{Al}$  MAS-NMR spectrum of a spinnable  $\text{Al}_2\text{O}_3$  precursor.

The spectrum of Fig. 2(a) reveals two peaks of similar intensity at 3 ppm and  $-10$  ppm, which both can be assigned to two types of six-fold coordinated Al-atoms. The upfield shift at  $-10$  ppm can be explained by an enhanced electron density surrounding a part of Al nuclei compared to  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ . We suppose that propionic acid solvates the Al compound and forms an addition compound with Al leading to a higher electron density. As a result the single molecule clusters can interact by hydrogen bondings between propionic acid and hydroxy groups, which enables the sol to get spinnable. The surface reactions between the particles in the sol state is depicted schematically in Fig. 3. By the enormous increase of surface after the spinning process the fibers lose propionic acid and solid gel fibers yield. Figure 1 (right) shows the IR spectra of all different gel fibers. Remarkable is the missing of the carbonyl band at  $1718\text{ cm}^{-1}$  and  $1740\text{ cm}^{-1}$ . The corresponding  $^{27}\text{Al}$  MAS-NMR spectrum of gel fibers of the  $\text{Al}_2\text{O}_3$  system reveals a clearly reduced

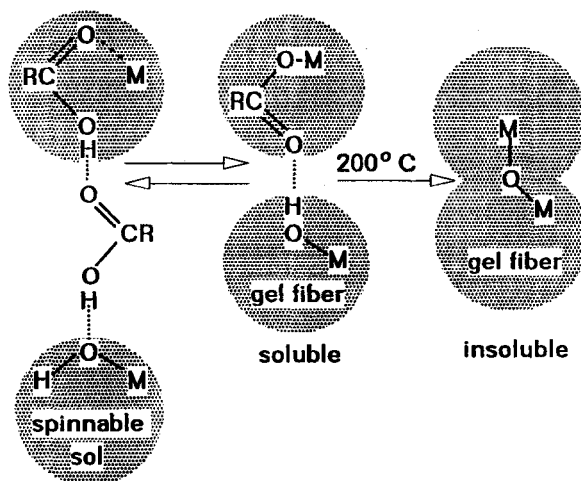


Figure 3. Suggested surface reactions between particles during sol-gel transition of spinnable precursors.

intensity of the upfield resonance which is only visible as a shoulder (Fig. 2(b)).

For all gel fibers of the systems studied a unique property can be observed. They are soluble in ethanol or propionic acid, even after heating them at  $80^\circ\text{C}$  for one hour. This leads to the conclusion that all these fibers consist of a reversible gel whose solid phase is stabilized by hydrogen bondings between monodentate carboxylates and hydrogen groups (see Fig. 3). This explains, why the gel can be converted back to the sol state. After dissolving the gels in ethanol Small Angle X-ray Scattering (SAXS) measurements reveal gyration radii, which range between 0.5 and 1.5 nm.

The reversible performing merely changes after heat treatment at about  $200^\circ\text{C}$ , when the fibers get insoluble.

In the  $^{27}\text{Al}$  MAS-NMR spectrum of gel fibers ( $\text{Al}_2\text{O}_3$  system) which were treated at  $200^\circ\text{C}$  only one signal is visible which can be assigned to six-fold coordinated Al. In addition, the NMR spectrum clearly reveals two further signals at 40 ppm and 75 ppm assigned to five- and four-fold coordinated Al-atoms, respectively. This is in accordance with observations of Wood et al. on hydrolyzed systems derived from aluminum salts and urea, which has been heated at  $200^\circ\text{C}$  [19]. The corresponding IR spectra of all gel fibers show a growth of those bands which can be assigned to the oxidic fraction after heat treatment. This indicates a stabilization of the solid phase in the gel fibers by oxo bridges (see Fig. 3). Bidentate carboxylates, however, are still present within the particles. Organic decomposition of fibers of all systems described is completed at about  $450^\circ\text{C}$  according to DTA measurements.

### 3.3. Conversion from Gel to Polycrystalline Fibers

The conversion of gel fibers to a solid polycrystalline oxide fiber that is free of organic moieties is critical in terms of crack formation. Due to the low solid yield of the gels high shrinkage of up to 85 vol% occurs during the conversion to polycrystalline fibers. This and the exothermic decomposition of carboxylates mainly between  $250^\circ\text{C}$  and  $300^\circ\text{C}$  necessitates special conditions during heat treatment. Low heating rates and a partial use of an inert atmosphere helps to suppress crack formation completely. In the case of PZT fibers this thermal treatment under inert atmosphere is especially critical, since  $\text{Pb}^{2+}$  will be reduced to elementary lead. The heat treatment therefore, requires the subdivision into several steps with different atmospheres to prevent reduction. Figure 4 shows a PZT fiber after

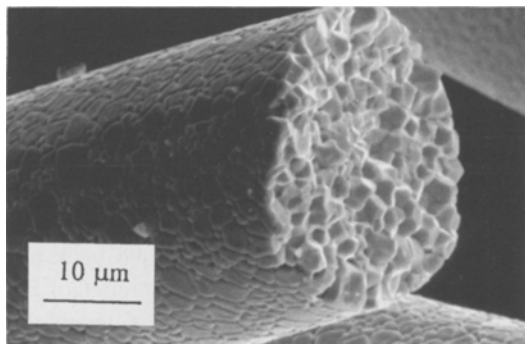


Figure 4. SEM micrograph of a typical fracture surface of a polycrystalline PZT fiber heated at  $950^\circ\text{C}$  for five hours.

heat treatment in  $\text{N}_2$  up to  $300^\circ\text{C}$ , in air to  $600^\circ\text{C}$  and under a high  $\text{PbO}$  partial pressure up to  $950^\circ\text{C}$ . The polycrystalline PZT fiber has a circular cross section with a diameter of  $30\ \mu\text{m}$ . The fracture surface reveals a homogeneous microstructure with an average grain size of about  $2.5\ \mu\text{m}$ . The fiber is crack free.

## 4. Conclusions

One appropriate way to form structural and functional ceramic long oxide fibers is the sol-gel process, because of its ability to design the molecular structures of metal oxide precursors leading to the forming of the resulting products in a spinning unit. Structural ceramic oxide fibers as spinel, YAG and eutectic composition of alumina and YAG as well as the functional PZT fibers could be achieved. All precursors are based on metal oxohydroxopropionates. A comparative study of sol-gel routes leading to spinnable sols demonstrated the key role of propionic acid as an excellent agent for controlling hydrolysis and condensation reactions. All these precursors derived from propionates allow continuous spinning on a pilot-plant scale. The conversion to polycrystalline fibers succeeded by using an inert atmosphere during decarboxylation. The metal propionates might be also useful for the preparation of thin layers.

## Acknowledgment

The authors gratefully acknowledge Mrs. M. Rothenburger-Glaubitt and Ms. M. Roth for the preparation of the novel precursors as well as Mr. F. Essl for helpful discussions.

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